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TRANSLATION

THERMAL DECOMPOSITION OF NITROSYL PERCHLORATE

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THERMAL DECOMPOSITION OF NITROSYL PERCHLORATE

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According to the data of Cruse, Huck and Moller [1], solid nitrosyl perchlorate completely decomposes to gaseous substances above 120° according to the equation

$$2NOClO_4 = N_2O_4 + Cl_2 + 3O_2.$$

The primary products of decomposition, in their opinion, are N_2O_5 and ClO_2 which then break down into nitrogen tetroxide, chlorine and oxygen. Heretofore the solid phase in the thermal breakdown of $NOClO_4$ was not known. It was assumed that it was entirely composed of still undecomposed nitrosyl perchlorate [1, 2].

The starting nitrosyl perchlorate we obtained by the action of N_2O_3 on an 80% solution of perchloric acid [3] and purified by holding in a vacuum at 50° in the presence of P_2O_5. The results of an analysis of the product obtained are: NO - 23.22%, Cl - 17.10%, total acidity - 1.995 eq/mole; calculated: NO - 23.18%, Cl - 27.39%, total acidity 2.000. All handling of the nitrosyl perchlorate was done in a dry chamber.

Decomposition of the nitrosyl perchlorate was carried out in a vacuum at a partial pressure of 1 mm Hg and at a temperature of 99 $\pm$ $\pm$ 0.1°. A weighed portion of the substance was first ground in an agate mortar and then spread in a thin layer on the flat bottom of a vessel for decomposition. The outgoing gases were condensed in a trap at the temperature of liquid nitrogen. The experiment was interrupted at various stages of decomposition and a complete analysis was made of the solid residue and of the condensed gases.

The results of analysis may be satisfactorily explained if it is assumed that together with the nitrosyl perchlorate, nitronium perchlorate NO_2ClO_4 is also in the solid material. In order to verify this assumption, an infrared spectrum of a suspension of the solid residue in mineral oil was taken. Along with the lines associated with the ion ClO_4, the spectrum revealed a line at 2293 cm^{-1} which is associated with the vibration of the NO^+ ion [4] and a line at 1385 cm^{-1} associated with the bond vibration of the linear ion NO_2^+ [5].

The ratio of chlorine to nitrogen in the gases in all experiments are nearly one. The composition of the material balance in each experiment made it possible to conclude that the chlorine and nitrogen are liberated to the gaseous phase as the dioxides ClO_2 and NO_2. In one experiment the condensed gases were dissolved in water and the absorption spectrum in the visible range of the green-yellow solution obtained was compared with the spectrum of a solution of pure chlorine dioxide. Comparison of the spectra indicated that chlorine dioxide is one of the products of decomposition of nitrosyl perchlorate. Together with ClO_2 there is a significant quantity of elemental chlorine. Apparently this is because the chlorine peroxide generated

in the hot zone of the apparatus decomposes to chlorine and oxygen. According to Schumacher and Stiger [6], this reaction proceeds at an appreciable velocity even at 30-50°.

Figure 1 shows the results of a study of the decomposition products of nitrosyl perchlorate. The quantities are expressed in moles of NO_2ClO_4, ClO_2 and NO_2 produced from one mole of starting nitrosyl perchlorate at various stages of decomposition. Curves of the accumulation of the end products ClO_2 and NO_2 as well as of the consumption of $NOClO_4$ have an S-shaped form, which is characteristic for the kinetics of thermal decomposition of solid substances. The quantity of nitronium perchlorate at first increases, passes through a maximum, and then gradually drops.

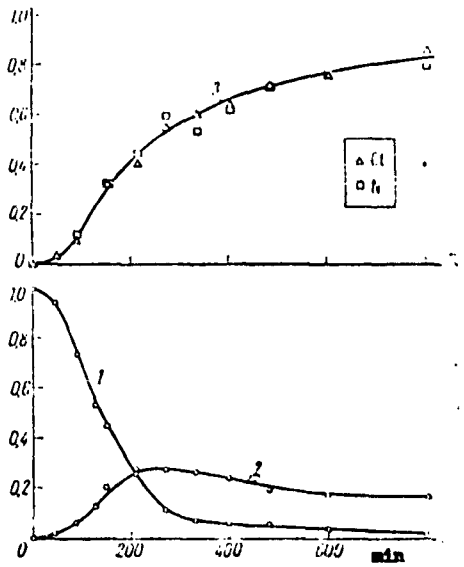

Fig. 1. Kinetics of decomposition of nitrosyl perchlorate at 99°, 1) $NOClO_4$; 2) NO_2ClO_4; 3) ClO_2 and NO_2.

From the shape of curve 2 (Fig. 1) we can conclude that two

consecutive reactions take place in the decomposition of nitrosyl perchlorate. The first is associated with the decomposition of nitrosyl perchlorate and the formation of nitronium perchlorate. The second is associated with the decomposition of the nitronium perchlorate

$$2NOClO_4 = NO_2ClO_4 + NO_2 + ClO_2 \qquad (1)$$

$$NO_2ClO_4 = NO_2 + ClO_2 + O_2. \qquad (2)$$

The ratio NO_2ClO_4:$NOClO_4$ in the solid phase increases during the course of the entire process, i.e., the rate of decomposition of nitrosyl perchlorate according to reaction (1) is somewhat greater than the rate of decomposition of the nitronium perchlorate according to reaction (2).

If the nitrosyl perchlorate is decomposed under conditions of continuous temperature rise, the two stages of the process can be separated in time. Figure 2 shows a thermogram of the heating of nitrosyl perchlorate under vacuum as recorded by a Kurnakov pyrometer. The thermograph exhibits two sharply separated endothermic effects the first of which, at a temperature of 100-125°, corresponds to the decomposition of nitrosyl perchlorate according to reaction (1) and the second, at a temperature of 165-180°, to the decomposition of the accumulated nitronium perchlorate according to reaction [2].

The results of the present work make it possible to conclude that the thermal decomposition of nitrosyl perchlorate proceeds in two stages with an intermediate formation of nitronium perchlorate, which is more stable than nitrosyl perchlorate.

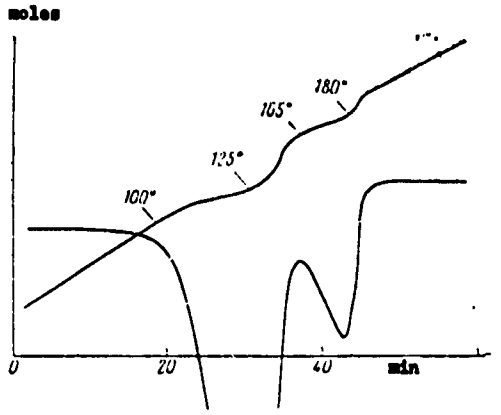

Fig. 2. Thermogram of the decomposition of nitrosyl perchlorate.

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